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<b>(54) Title:</b> A BIAXIALLY ORIENTED TWO-LAYER COPOLYESTER FILM FOR CAPACITOR DIELECTRIC USE		
<b>(57) Abstract</b> <p>The present invention comprises a two-layer biaxially oriented copolyester film useful for capacitor dielectrics. Such films have good winding characteristics, slipperiness, good mechanical properties, and excellent thermal stability. The two-layer biaxially oriented copolyester film comprises: (a) a two-layer biaxially oriented copolyester film, wherein at least one layer essentially consists of PENBB and which two-layer biaxially oriented copolyester film has a melting point sufficient to withstand a thermal treatment of about 260 °C for about 10 seconds or higher; and (b) an effective amount of one or more particulate materials uniformly dispersed in at least one layer of said two-layer biaxially oriented copolyester film sufficient to provide slip and good winding characteristics, whereby the average surface roughness <math>R_a</math> of one of said layers is <math>\leq 10</math> nm and that of the other layer is <math>&gt; 10</math> nm.</p>		

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A BIAXIALLY ORIENTED TWO-LAYER COPOLYESTER FILM  
FOR CAPACITOR DIELECTRIC USE

Background Of The Invention

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(1) Field Of The Invention

This invention relates to a two-layer biaxially oriented copolyester film having low shrinkage properties and good thermal properties for use as a capacitor dielectric film. In particular, the film of the present invention must have good winding characteristics as well as slipperiness to permit the film to slide over a previously wound section (i.e., to be non-blocking) while also having minimum layer-to-layer distance. In addition to the above characteristics, the film of the present invention has good mechanical strength, especially stiffness (tensile modulus) and thus thickness reduction can be achieved, making the film of the present invention exceptionally useful as a capacitor dielectric.

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(2) Prior Art

Many prior art documents profess to disclose a satisfactory polymeric film capable of being employed as a material for capacitors. However, there are no commercially available films which have the outstanding properties of the present invention. Chiefly lacking in the prior art films is thermal stability. Thermal stability is important because with surface mounting assembly a capacitor incorporating the dielectric film must be dipped in a solder bath at approximately 260°C to solder the leads of the capacitor to a circuit board. The majority of the prior art films fail due to melting and/or shrinking during or shortly after exposure to a solder bath. Because the yield in such a process is particularly low, the cost of the circuits using these film capacitors is so high as to be prohibitive. The circuit manufacturer must make do with ceramic capacitors, which have inferior dielectric properties.

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Similar properties with respect to thermal stability and mechanical strength (stiffness) at low thickness are also required for improved base film for thermal transfer printing ribbon in order to provide sharp printed images at high speed and large cassette tape capacity. Therefore, easily windable film suitable for capacitor dielectric is also useful as thermal transfer ribbon base.

Another desired characteristic of capacitor dielectric films is a low water pickup. Low water pickup is important because this retards the degradation of the capacitor due to corrosion of the metallized layer. With the present invention, a film water pickup at 23°C and 50 % r.h. of less than 0.1 weight-% and preferably less than 0.06 weight-% are possible.

European Patent Application No. 423,402 filed October 17, 1989 by Katoh et al, discloses a thermal plastic polymeric film said to have usefulness as a material for capacitors and for thermal transfer ribbons. This patent discloses that the polymeric substrate can be polyester, polyphenylene sulfide, polyamides, polysulfones, and polyvinylidene fluoride. While some of these polymers have good thermal characteristics, they are either very expensive to produce, have relatively poor mechanical properties or relatively high moisture pick-up that make their usefulness for capacitor films or thermal transfer ribbons impractical.

In an attempt to make polymers more thermally stable and particularly polyester polymers, copolymers of polyethylene naphthalate/4,4'-dimethyl bibenzoate are described below.

U.S. Patent No. 3,008,934 discloses copolyesters containing as acid derived units 4,4'-bibenzoate and a host of other dicarboxylates including 2,6-naphthalic dicarboxylate. It also discloses oriented fibers and films prepared from these copolyesters, however, biaxially oriented PENBB films are not disclosed or envisioned. In particular, those films with improved stiffness (tensile modulus) and tensile strength in both MD and TD as well as thermostability, UV stability, hydrophobicity, dimensional stability and impermeability toward gases in comparison to PET film are not disclosed in U.S. Patent No. 3,008,934.

Japanese Patent No. 50.135333 to Teijin Limited describes a fiber material composed of a copolyester of polyethylene naphthalate with 0.5 to 20 mole-% 4,4'-dimethyl bibenzoate content higher than 20 mole-% is disadvantageous because the melting point (about 237°C) of the resulting polymer is significantly below that of polyethylene terephthalate (PET) polyester (meaning that the thermal stability is also lower). Specifically, this patent teaches that a very small mole-% of 4,4'-dimethyl bibenzoate (0.5 to 3 mole-%) in poly-2,6-naphthalate results in a melting point higher than PET and thus yields better thermal stability during processing. Therefore, as the percentage of 4,4'-dimethyl bibenzoate increases, the melt point, and thus thermal stability, decreases according to this reference.

There continues to be a need for a thermoplastic polymer having excellent thermal stability characteristics and having the requisite mechanical strengths, especially improved stiffness (tensile modulus) sufficient to permit those skilled in the art to produce a film capable of being employed as a capacitor film.

#### Summary Of The Invention

The present invention relates to a biaxially oriented PENBB copolyester film having at least about 25 mole-% of the diacid or diester content in the copolymer of 4,4'-bibenzoic acid or of 4,4'-dimethyl bibenzoate with the remainder of the copolyester being produced from a different diacid or diester. The copolyester must have a melting point sufficient to permit the copolymer to withstand a solder bath such as those known in the capacitor dielectric manufacturing industry, i.e., the copolyester film must not melt or shrink.

With the present invention, shrinkages of less than 0.5 % at 150°C are possible, preferably films having a shrinkage of equal to or less than 0.3 % are possible.

Furthermore, a copolyester film useful for capacitor dielectrics must also have good winding characteristics, slipperiness, as well as the mechanical strength, especially stiffness to form an ultrathin film. The reason thickness

reduction of polymeric films employed for dielectric material in a capacitor is advantageous because the electrostatic capacitance of the capacitor is proportional to the dielectric constant of the dielectric material and inversely proportional to the square of the thickness of the film. If the dielectric material is constant,  
5 reducing the thickness of the film makes the production of capacitors of a smaller size and a larger capacity possible.

In addition to thickness, it is necessary for films used in capacitors to have good handling characteristics. Neat polyester films generally do not slide with respect to themselves. In fact, such films usually produce blocking in which  
10 layers of the film refuse to slide over one another unless an unnecessarily high force is employed. Such a force often scratches or destroys the flatness of the film and sometimes even causes breakage. In order to provide sufficient slip and good winding characteristics of a film, it is known to employ fine protrusions or depressions on the surface of the film. Such protrusions or depressions on the  
15 surface of the film are made by incorporating into the thermoplastic polymer fine inert filler particles. Such characteristics may be achieved with a bimodal particle distribution. Such filler particles are disclosed in the above identified European Patent Application No. 423,402.

In one embodiment, a bimodal particle distribution of filler material can be  
20 employed to provide sufficient slip and good winding characteristics. These particles may also be in the form of agglomerated fine particles which, upon blending with the polymer resin and subsequent film processing, break up into finely divided particles.

To further increase the capacitance of a capacitor at a given size, it is also  
25 advantageous to reduce the distance between the individual layers of the ultra thin metallized dielectric film. This can be achieved without deteriorating the slip and winding characteristics of the film by providing a dual layer biaxially oriented copolyester film wherein layer A is essentially smooth and only layer B is roughened to facilitate slip and winding. Such rough/smooth bilayer copolyester  
30 films can be produced by coextruding a copolyester layer A containing either no

particulate matter at all or only very fine particles together with a copolyester layer B containing sufficient particles or larger particles to facilitate winding. The particles may be added in a range from 0.01 to 5 parts by weight, based on the weight of the copolyester, and have an average particle diameter of about 0.01 to about 5  $\mu\text{m}$ . The  $R_s$  value of layer A should be  $\leq 10$  nm and the  $R_s$  value of layer B should be  $> 10$  nm.

In the broadest sense, the present invention comprises a biaxially oriented PENBB copolyester film useful for capacitor dielectrics or thermal transfer printing ribbon base, wherein the biaxially oriented copolyester film has at least 25 mole-% of the diacid or diester content of 4,4'-bibenzoic acid, or 4,4'-dimethyl bibenzoate ester, and having a melt point sufficient to withstand a thermal treatment of at least about 260°C or higher for about 10 seconds; and incorporating into the copolyester on at least one side of the film an effective amount of one or more fillers sufficient to provide slip and good winding characteristics.

#### Brief Description Of The Drawing

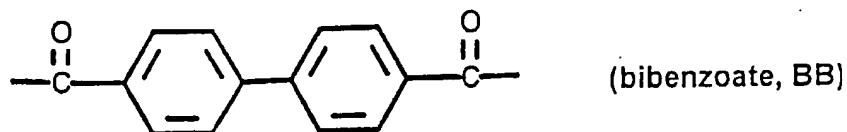
Figure 1 is a graph showing the dependence of the melting point temperature of the preferred PENBB copolyester, based on 2,6-naphthalate and 4,4'-bibenzoate on its molar diacid ratio.

#### Description Of The Preferred Embodiments

Generally the PENBB copolyesters of the present invention are made by reacting at least two dicarboxylic acids, or their ester equivalents with suitable glycols or diols, as is well known in the art. Such a reaction produces monomers or oligomers of the copolyester. The monomers or oligomers are then subject to a polycondensation reaction, as known in the art, to produce a copolyester.

The PENBB copolyester of the present invention is derived primarily from dicarboxylic acids or their ester equivalents with at least 25 mole-% of the dicar-

boxylic acid being 4,4'-bibenzoic acid (or the ester equivalent) having the following formula:



The remainder of the copolyester may be formed from other dicarboxylic acids or their ester equivalents, such as terephthalic acid, isophthalic acid, phthalic acid, naphthalene-2,6-dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid, di-(4-phenyl)-acetylene dicarboxylic acid, 1,2-di-(4-phenyl)-ethylene dicarboxylic acids, sebacic acid, malonic acid, adipic acid, azelaic acid, glutaric acid, suberic acid, succinic acid, and the like, or mixtures of these can be employed in the present invention. Naphthalene-2,6-dicarboxylic acid is the preferred remainder diacid.

Suitable diols employed in the present invention include ethylene glycol, diethylene glycol, propylene glycol, butanediol, 1,5-pentaediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, cyclohexane dimethanol, and the like. Ethylene glycol is the preferred glycol.

Suitable copolyesters of the present invention can comprise, for example, polyethylene terephthalate/4,4'-bibenzoate, polybutylene terephthalate/4,4'-bibenzoate, polypropylene terephthalate/4,4'-bibenzoate, polyethylene naphthalate/4,4-bibenzoate, polyethylene terephthalate/isophthalate/4,4'-bibenzoate, polyethylene terephthalate/adipate/4,4'-bibenzoate, polyethylene terephthalate/sulphoisophthalate/4,4-bibenzoate, and the like.

In order to achieve the desired mechanical properties in the biaxially oriented PENBB film it is recommended that the IV value (inherent viscosity, as measured in a 1 : 1 weight-ratio mixture of pentafluorophenol and hexafluoroisopropanol at a concentration of 0.2 g/dl and a temperature of 25 °C) of the PENBB polymer after extrusion be > 0.5 dl/g and preferably > 0.55 dl/g.



In a preferred embodiment, a polyethylene naphthalate bibenzoate copolyester comprises roughly equimolar portions of the esters ethylene naphthalate and 4,4'-bibenzoate, or the acids of naphthalene-2,6-dicarboxylic acid and bibenzoic acid. The copolyester is obtained by polycondensation of the diacids or diesters with a diol. It may be advantageous, however, to employ an excessive amount of the diol in order to influence the reaction kinetics. After the reaction of the diacids or diesters with the diol, a polycondensation preferred embodiment, a mixture of two or more dicarboxylic acids or esters are mixed with at least of two or 100 mole-% of the corresponding diol. The diacids or their ester equivalents and the diols are mixed uniformly and heated to approximately 200°C in the presence of a transesterification catalyst, as is well known in the art. The reaction yields monomer or low molecular weight polyester which is subsequently subjected to the polycondensation reaction in the presence of a polycondensation catalyst. Additionally, stabilizers, antioxidants, delustrants, pigments, fillers, antistatic agents, etc., may be uniformly mixed with the copolyester. The addition of particulate matter is - insofar as it is inert - preferably performed in an ethylene glycol slurry before, during or immediately following the ester formation or transesterification and at all events before the polycondensation. This addition in a less viscous state enables improved dispersion of the particulate matter.

Suitable catalysts are antimony, manganese, cobalt, magnesium, zinc, calcium, etc., as are well known in the art. The preferred transesterification catalyst, where employed, would be manganese and/or cobalt. The preferred polycondensation catalyst would be antimony compounds. Such catalysts are well known and conventional in the prior art.

The two-layer biaxially oriented copolyester film of the present invention can be manufactured by a coextrusion process, where the copolyester resin composition A containing no or only very fine particulates and copolyester resin composition B containing larger particles are heated to a molten state in separate extruder and then combined in a combining block or dual manifold die and

extruded in the form of a two-layer amorphous sheet onto a polished, revolving casting drum. The amorphous sheet is rapidly cooled or "quenched" to form a cast sheet of polyester. The cast polyester sheet is removed from the casting drum and then axially stretched in one direction, either in the direction of the film travel (machine direction, MD) or perpendicular to the machine direction (transverse direction, TD), while being heated to a temperature between the glass transition temperature and about 30°C above the cold crystallization temperature (both temperatures can easily be measured on the films by differential scanning calorimeter (DSC)).

5 The copolyester film of this invention is biaxially oriented, i.e. stretched in both the machine direction and the transverse direction. The total stretch ratios in the machine direction and the transverse direction lie between 1:2 and 1:10, preferably between 1:2.5 and 1:5. The product of the total stretch ratios should be between 1 to 30, and preferably between 5 to 20. Biaxial drawing is performed such that the birefringence is < 0.2, preferably < 0.1 to ensure adequately isotropic properties. Birefringence as mentioned herein is the absolute value of the difference between the maximum and minimum refractive indices in the plane of the film, as measured on common instruments such as Abbé refractometer, optical bench or compensators.

15 After orientation of the film, a heat setting step takes place to lock in the properties of the film. The heat setting occurs at a temperature between the cold-crystallization temperature and the melt temperature of the copolymer composition. After heat setting, the film may be wound on a roll, or in some cases surface treatment of the film such as corona treatment, plasma or flame treatment may be employed before winding the film on the roll, particularly where the film will be further coated with a primer coating or a metallic coating, for example.

20 It is desirable for the film to have a final total thickness of between 0.1 and 12  $\mu\text{m}$ , preferably between 0.3 and 6  $\mu\text{m}$ .

No matter what copolyester composition is employed, it must be able to withstand a solder bath which is typically in the range of about 260°C for about 10 seconds. Copolyesters which can survive this conditioning are thermally stable for the present invention. Copolyesters of the present invention typically have a melting point dependent upon the composition. Figure 1 illustrates a melting point curve based on a preferred composition of PENBB. Similar curves are also expected for other copolyesters of the present invention.

To further increase the capacitance of a capacitor of a given size, it is also advantageous to reduce the distance between the individual layers of the ultra thin metallized dielectric film.

This can be achieved without deteriorating the slip and winding characteristics of the film by providing a dual layer biaxially oriented copolyester film wherein layer A is essentially smooth and only layer B is roughened to facilitate slip and winding. Such rough/smooth bilayer biaxially oriented copolyester films can be produced by coextruding a copolyester layer A containing either no particulate matter at all or only very fine particles together with a copolyester layer B containing sufficient particles or larger particles to facilitate winding. The particles may be added in a range from 0.01 to 5 parts by weight, based on the weight of the copolyester, and have an average particle diameter of about 0.01 to about 5  $\mu\text{m}$ . The  $R_s$  value of layer A should be  $\leq 10$  nm and  $R_s$  value of layer B should be  $> 10$  nm.

In order to provide good handling and winding properties, the film composition must be such that one surface is rough. This is achieved by incorporating inert insoluble particles into one or both layers of the film. Layer A, which is essentially smooth, contains no or only very fine particles. Layer B, which is rough, contains particles. In the case that layer A also contains particles, those in layer B are larger. Layer B may also contain particles with a bimodal particle size distribution in which case it is possible that the finer particles are the same size as the optional fine particles layer A. The fine inert insoluble particles can be in the form of an agglomerate which disperses or breaks up upon orientation

of the film to form fine inert insoluble particles. Generally, these particles may be added to the raw materials or more preferably to the monomers before or during polycondensation or to the polymer before extrusion. Such inert particles either in agglomerated form or finely dispersed powders can be kaolin, talc, silica, carbonates of magnesium, calcium, or barium; sulfates of calcium, or barium; phosphates of lithium, calcium, or magnesium; oxides of aluminum, silicon, titanium, zirconium, or mixtures thereof, lithium fluoride, carbon black, or the organic acid salts of calcium, barium, zinc, and manganese. It is also possible to use fine particles made of crosslinked polymers such as polystyrene, polyacrylate, or polymethacrylate, for example, which are inert with respect to the reactions described herein to make the copolyester.

The particles may be of one type or mixtures of several types. The shapes of the particles can be irregular, flaky, spherical, or elongated. Preferably, spherical particles are employed particularly for the large particles. The hardness, density and color of the particles is generally immaterial. The average size of the particle should be less than 10  $\mu\text{m}$ , and generally preferably less than 3  $\mu\text{m}$  as will be discussed later. The amount of particles incorporated into the film should generally be in a range of from 0.01 % to 5 % by weight and preferably between 0.5 % and 2.0 % by weight.

For one of the embodiments of the present invention, is preferable to have a bimodal particle distribution, i.e. particles of a large size distribution and particles of a small size distribution.

The bimodal particle distribution for the present invention comprises from about 0.01 to about 3 % by weight of inert particles having an average particle diameter of 3 to 50 nm which optionally may be aggregates of the fine particles, said aggregates having an average particle diameter of 0.05 to 5  $\mu\text{m}$ . The other modal particle distribution consists of 0.005 to 1 % by weight having an average particle diameter of 0.05 to 4  $\mu\text{m}$  and are preferably spherical with an aspect ratio of from 1.0 to 1.2.

The content of the fine inert particles should be in a range from 0.01 to 3 % by weight based on the weight of the copolyester. If the content is less than 0.01 % by weight, the excess air is trapped between the layers upon winding. On the other hand, if the fine particle mixture exceeds 3 % by weight, the films surface is excessively roughened and the dielectric breakdown voltage of the film is decreased. The larger particles are more spherical in shape and differ from the ultra fine lumpy particles. The larger particles have a particle size of about 0.5  $\mu\text{m}$  to 4  $\mu\text{m}$  and employed in a range of 0.005 to 1% by weight, based on the weight of the copolyester. Preferably, the average particle diameter of the large particles is not larger than the thickness of the film. Preferably, the large particle diameters size is between about 0.2 and 3  $\mu\text{m}$ . If the large particle size is less than 0.05  $\mu\text{m}$ , the resulting film has insufficient slipperiness and cannot be handled easily. If it exceeds 4  $\mu\text{m}$  in size, the surface of the film is excessively rough and the dielectric breakdown voltage is decreased and insulation defects increase.

The bimodal particle distribution described in the present invention is generally similar to that described in European Patent Application No. 423,402, as previously described. With the present invention, however, it is contemplated that a broader range (types) of inert particles can be employed for both the fine particle size and the large particle size.

For the purpose of this invention the following measurement methods were used:

#### IV - Inherent Viscosity

The solution viscosity of a 0.1 or 0.2 weight-% solution of the PENBB copolyester in a 1:1 mixture by weight of pentafluorophenol and hexafluoroisopropanol was determined by capillary viscosimetry in an Ubbelohde viscosimeter. The IV was calculated from the following relation:

$$IV = \frac{\ln(\eta_{rel})}{c} \quad 12$$

wherein  $\eta_{rel} = \frac{\text{solution viscosity}}{\text{solvent viscosity}}$

c = concentration of solute in g/dl.

5

#### Mechanical Properties

The tensile properties of the film were determined in a tensile tester produced by Zwick (Ulm, Germany). The test parameters were

10	testing length	:	100 mm
	sample size	:	200x15 mm
	draw rate (modulus)	:	10 %/min
	draw rate (other values)	:	100 %/min

#### 15 Aspect Ratio of Particles

The aspect ratio of a non-spherical particle is determined by dividing the length of the longest axis through the particle  $A_l$  by the length of the shortest axis perpendicular to  $A_l$ ,  $A_s$ .

$$\text{Aspect ratio} = \frac{A_l}{A_s}$$

20

The values  $A_l$  and  $A_s$  can be determined by microscopy, such as SEM.

Water Pick-Up at 50 % r.h.

The film sample is conditioned at 50 % relative humidity and 25 °C for  $\geq$  2 days. It is then quickly placed in a commercial coulometric water tester manufactured by Du Pont. The sample is heated under a dry stream of  $N_2$  until  
5 no more water is desorbed by the sample. The desorbed water in the  $N_2$  stream is absorbed onto  $P_2O_5$  and the amount is determined coulometrically, using the calibration constant of the instrument determined daily with a known sample.

The following examples serve to illustrate the present invention, without limiting its scope.

Measurement Of Roughness  $R_a$ 

The  $R_a$  value gives the surface roughness in the form of the arithmetic average of all displacements of the roughness R from the center line. The measurement is performed according to DIN standard 4768 on a surface tester  
15 (Perthometer SPG made by Feinprüf GmbH of Gottingen, Germany). The values given are based on 6 individual measurements, in which the highest value is discarded before averaging. The cut-off, i.e. individual length of the measurement sections, is 0.08 mm.

## EXAMPLE 1

(preparation of neat copolyester)

289 parts by weight of dimethyl 2,6-naphthalene dicarboxylate, 322 parts by weight of dimethyl 4,4'-bibenzoate, 368 parts by weight of ethylene glycol and 0.7 parts of manganese acetate tetrahydrate are introduced into a  
25 conventional polycondensation reactor provided with a blanketing gas line ( $N_2$ ), pressure equalization, a thermometer, a condenser, a vacuum line and stirred for 2.5 hours, during which time methanol distills off. 0.675 parts by weight of triphenyl phosphate and 0.2259 parts of antimony trioxide are then added as polycondensation catalysts and the mixture is heated to 270°C, with stirring.

Vacuum is applied and the temperature is raised to 285°C and maintained for 2.5 hours.

5 The residual melt is granulated. The granules are white, opaque and crystalline. An IV value of 0.56 dl/g was determined for the granules (measured at a concentration of 0.1 g/ml in pentafluorophenol/hexafluoroisopropanol [weight ratio 1:1] at 25°C).

The granules are further condensed for 20 hours at 240°C under vacuum in the solid phase. After this treatment the IV value is 1.1 dl/g. The melting point ( $T_m$ ) is 281°C.

10

## EXAMPLE 2

(preparation of copolyester with particulate filler)

15 The same procedure as in Example 1 is followed, except that 23 parts of a slurry of BaSO<sub>4</sub> particles in ethylene glycol is added to the transesterified mixture just before adding the triphenyl phosphite and antimony trioxide. This slurry is prepared by dispersing 10 parts by weight of BaSO<sub>4</sub> with an average particle diameter of 0.6  $\mu$ m in 30 parts by weight of ethylene glycol. The resulting copolyester contains 0.3 wt.-% BaSO<sub>4</sub> particles.

20

## EXAMPLE 3

25 The copolyesters prepared according to examples 1 and 2 are each melted in separate extruders, sent to a multimanifold slot die via 2 gear pumps running at equal throughput, combined to form a two-layer film, cooled on a chill roll to 20 °C. The thus obtained amorphous film is heated to 125°C and drawn by a factor of 3.5 in MD, then TD. The film is then heat set under restraint at 260°C for 10 seconds to afford a two-layer biaxially oriented copolyester film 8 $\mu$ m thick with a rough and a smooth side, which can be wound with no difficulty.



The mechanical properties are:

	MD	TD	Unit
tensile modulus	9.2	8.0	GPa
tensile strength	240	180	MPa
elongation at break	25	7	%

The  $R_a$  values of each side were:

rough side:	15	nm
smooth side	4	nm

The shrinkage, measured after 15 min. treatment in a forced air oven at 150°C is 0.3% in both MD and TD. The water pickup of the film at 50 % r.h. and 25 °C is 0.04 %.

#### EXAMPLE 4

(comparative)

A monolayer film is prepared from the copolyester according to Example 1 in a manner similar to example 3, except that only one extruder is used. After drawing, it is not possible to wind this film due to wrinkles and blocking.

The roughness  $R_a$  of a portion of the film is:

side A	4	nm
side B	4	nm

Thus, it is apparent that there has been provided, in accordance with the invention, a biaxially oriented copolyester film useful as a capacitor dielectric film

or as a thermal transfer ribbon film, that fully satisfy the objects, aims, and aspects set forth above. While the invention has been described in conjunction with the specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light  
5 of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the sphere and broad scope of the present invention.

## THAT WHICH IS CLAIMED IS:

1. A two-layer biaxially oriented copolyester film comprising:
  - (a) a two-layer biaxially oriented copolyester film, wherein at least one  
5 layer essentially consists of PENBB and which two-layer biaxially oriented  
copolyester film has a melting point sufficient to withstand a thermal treatment  
of about 260°C for about 10 seconds or higher; and
  - (b) an effective amount of one or more particulate materials uniformly  
dispersed in at least one layer of said two-layer biaxially oriented copolyester film  
10 sufficient to provide slip and good winding characteristics, whereby the average  
surface roughness  $R_s$  of one of said layers is  $\leq 10$  nm and that of the other layer  
is  $> 10$  nm.
2. The biaxially oriented copolyester film of Claim 1 in which both layers  
15 essentially consist of PENBB.
3. The biaxially oriented copolyester film of Claim 1 or 2 in which the PENBB  
is selected from the class consisting of polyethylene terephthalate 4,4'-  
bibenzoate, polybutylene terephthalate 4,4'-bibenzoate, polypropylene terephth-  
20 halate 4,4'-bibenzoate, polyethylene naphthalate 4,4'-bibenzoate, polyethylene  
terephthalate/isophthalate/4,4'-bibenzoate, polyethylene terephthalate/adipa-  
te/4,4'-bibenzoate, polyethylene terephthalate/sulphoisophthalate/4,4'-bibenzoate.
4. The biaxially oriented copolyester film of Claim 3, wherein the PENBB is  
25 polyethylene naphthalate/4,4'-bibenzoate.
5. The biaxially oriented copolyester film of Claim 3, wherein said poly-  
ethylene naphthalate 4,4'-bibenzoate copolyester is produced from ethylene  
glycol, 40 to 60 mole-% of naphthalene-2,6-dicarboxylic acid and 60 to 40 mole-

% of 4,4'-bibenzoic acid or their ester derivates, said mole-% relating to the ratio of the acid derivative compounds.

5 6. The biaxially oriented copolyester film of any one or more of the preceeding Claims, wherein said one or more particulate material(s) has a bimodal particle distribution having:

(a) fine particles of 0.01 to 3 % by weight, based on the weight of said copolyester, and having an average particle diameter of 30 to 500 Å, and

10 (b) 0.005 to 1 % by weight, based on the weight of said copolyester, of large generally spherical inert particles having an average particle diameter of about 0.05 to 4 μm and an aspect ratio of from 1.0 to 1.2.

7. The biaxially oriented copolyester film of Claim 6, wherein said particles are selected from the class consisting of kaolin, talc, silica, carbonates of  
15 magnesium, calcium, or barium; sulfates of calcium or barium; phosphates of lithium, calcium or magnesium; oxides of aluminum, silicon, titanium, zirconium, and mixtures thereof; lithium fluoride, carbon black, and the organic acid salts of calcium, barium, zinc, and manganese; and crosslinked polymers.

20 8. The biaxially oriented copolyester film of Claim 6 or 7, wherein said fine particles and said large spherical particles are in different layers of said two-layer biaxially oriented copolyester film.

25 9. The biaxially oriented copolyester film of Claim 6 or 7, wherein both said fine and said large particles are in the same layer of said two-layer film.

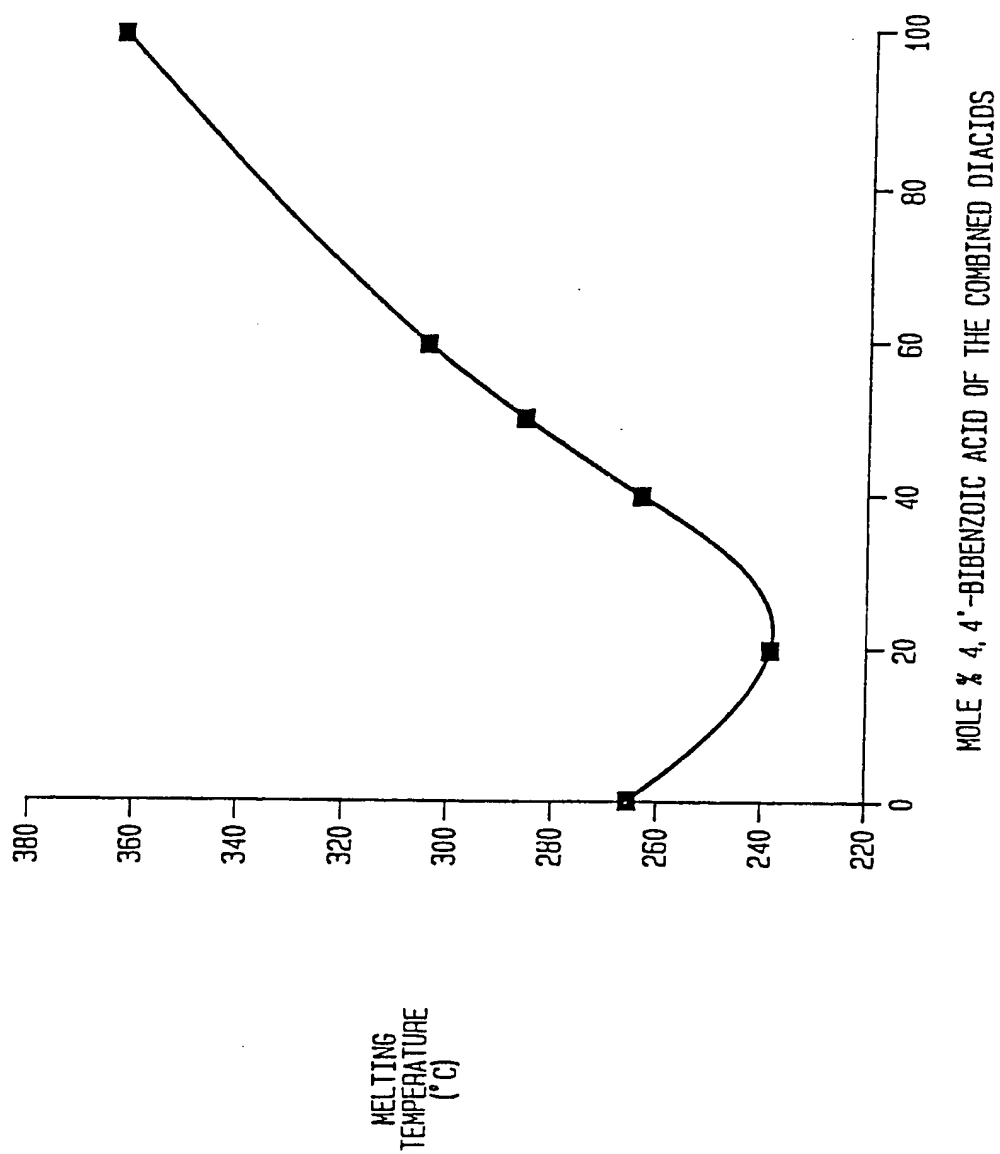
10. The biaxially oriented copolyester film of Claim 9, wherein the layer which does not contain both particles includes said five particles.

11. The biaxially oriented film of any one or more of the preceding claims, wherein the birefringence is  $< 0.2$  and the IV of the PENBB is  $> 0.5$  dl/g.

12. Use of a biaxially oriented copolyester film of any one or more of Claims 1 to 10 for capacitor dielectrics.

13. Use of a biaxially oriented copolyester film of any one or more of Claims 1 to 10 for thermal transfer printing ribbons.

FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10709

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B32B 33/00; DO6N 7/04

US CL :428/141, 143, 145, 147, 323, 325, 446, 480, 910

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/141, 143, 145, 147, 323, 325, 446, 480, 910

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,568,599 (ONO) 04 FEBRUARY 1986, entire document.	1-5
Y	US, A, 4,619,869 (KIRIYAMA) 28 OCTOBER 1986, entire document.	1-5
Y	US, A, 4,833,024 (MUELLER) 23 MAY 1989, entire document.	1-5
Y	US, A, 5,096,773 (SAKAMOTO) 17 MARCH 1992, entire document.	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 24 FEBRUARY 1993	Date of mailing of the international search report 13 APR 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer ELIZABETH EVANS Telephone No. (703) 308-2351

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/10709

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☒ Claims Nos.: 12,13  
because they relate to subject matter not required to be searched by this Authority, namely:  
  
Claims 12 & 13 are directed to a "USE" PCT Article 17(2)(a)(i). "Use" claims not in method terminology is not searched by this ISA.
2. ☐ Claims Nos.:  
  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-13  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.